

# Sorption of Low Levels of Nonionic and Anionic Surfactants on Soil: Effects on Sorption of Triticonazole Fungicide

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**Abstract:** The sorption of two anionic surfactants and a series of seven nonionic alkylphenoethoxylate surfactants of increasing hydrophilic/lipophilic balance (HLB) in a loamy clay soil was evaluated. The effect of low doses of these surfactants on the sorption characteristics of the fungicide triticonazole was investigated. The critical micellar concentration (CMC) of the surfactants in pure water and soil–water systems, and surfactant sorption were estimated by surface tension measurements using a batch equilibration technique. Triticonazole sorption, alone and in the presence of low doses of surfactants, was also measured by batch equilibration. CMC of the alkylphenol surfactants increased with their HLB. The sorption of surfactants increased with their lipophilicity. CMC in the soil–water systems were considerably higher than in pure water. Sorption of the most lipophilic alkylphenol surfactants at the higher doses significantly increased triticonazole sorption. Proposed mechanisms are modifications of soil surface properties, and increase of soil organic carbon content. Sorption of the other nonionic and anionic surfactants only resulted in monomeric surfactant concentrations in pore water, and did not affect triticonazole sorption. © 1998 Society of Chemical Industry

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## 1 INTRODUCTION

Triticonazole is a triazole systemic fungicide used for cereal seed treatment. The efficacy of systemic pesticides applied in seed treatments depends closely on their dissipation and localization in soil in relation to uptake by plant roots. The transport and fate of these molecules in soils are therefore of crucial interest for optimal utilization.

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Sorption of pesticides to the soil is a key process governing their behaviour in soils. Hydrophobic pesticides are strongly retained to soil through non-specific hydrophobic interactions with soil organic constituents, which significantly reduce their mobility in soils,<sup>1,2</sup> and their bioavailability to plants<sup>3,4</sup> and micro-organisms.<sup>5,6</sup> Sorption of organic chemicals may be modified by the presence of co-solutes. Surfactants are commonly used in commercial formulations of pesticides as humectants, dispersants or spreaders. It is thus essential to determine how sorption of a particular pesticide is affected by the presence of surfactant adjuvants when they co-exist in soil.

In soil–water systems, surfactant-pesticide interactions are very complex, and surfactant sorption as

well as pesticide sorption needs to be considered. Numerous studies have dealt with the influence of surfactants on the solubilization and sorption of poorly soluble contaminants in soil, and mobilization of strongly sorbed chemicals is often reported.<sup>7-9</sup> However, in most cases, high amounts of surfactant were used, which may be applied for decontamination of polluted soils, but would not be representative of amounts applied in pesticide formulations. Indeed, only limited amounts of formulation additives are applied with the active ingredient for treatment, and these will further dissolve and be diluted in the soil solution. The impact of low, diluted doses of surfactants thus needs to be considered more thoroughly.

The chemical nature of the surfactant is particularly relevant.<sup>10,11</sup> Nonionic surfactants are usually more efficient at solubilizing hydrophobic compounds than cationic or anionic compounds because they tend to form micelles at lower concentrations.<sup>12</sup> On the other hand, cationic and nonionic surfactants would sorb onto soil to a greater extent than anionic surfactants.<sup>9</sup> Alkylphenolethoxylate nonionic surfactants (denoted  $C_xPE_y$ , where  $x$  is the number of carbons of the alkyl chain, and  $y$  is the number of ethoxylate units) have been extensively studied, and reported to solubilize high amounts of pesticides,<sup>13</sup> and to reduce significantly their sorption.<sup>14-16</sup> The hydrophobicity of these surfactants varies with their alkylphenol hydrophobic moieties, and with the number of ethoxylate hydrophilic moieties. It is characterized by the hydrophilic-lipophilic balance (HLB), which is calculated from the percentage of hydrophilic ethoxylate units in relation to the total mass of the surfactant. The number of ethoxylate units and the HLB of these surfactants have been related to their sorption onto soil,<sup>17</sup> and to their ability to solubilize hydrophobic compounds.<sup>8,11,18</sup>

This study was aimed at (1) evaluating the influence of the HLB of selected nonionic alkylphenol surfactants on their micellization in water and soil-water systems, and on their sorption onto soil and (2) evaluating the impact of low doses of these surfactants and of two anionic surfactants used in the commercial formulation of triticonazole fungicide on its sorption onto soil.

## 2 MATERIALS AND METHODS

### 2.1 Chemical

[Benzyl- $U$ - $^{14}C$ ]triticonazole (specific activity: 1184 MBq mmol<sup>-1</sup>; radiopurity >98%) was provided by Rhône-Poulenc Agrochemicals Company (Lyon, France). Triticonazole water solubility is 8.4 mg litre<sup>-1</sup> at 20°C, vapour pressure is <10<sup>-8</sup> hPa at 50°C and distribution coefficient between octanol and water is 1950. Water solutions of [ $^{14}C$ ]triticonazole were pre-

pared at five different concentrations ranging from 0.5 to 5 mg litre<sup>-1</sup> by diluting a water solution of non-labelled triticonazole (analytical standard, purity >92%), and adding a few microlitres of the [ $^{14}C$ ]triticonazole methanol stock solution. Triticonazole concentrations were measured at 262.5 nm with a UV-visible Lambda V-Perkin Elmer spectrophotometer. The radioactivity was measured by liquid scintillation counting using a Kontron Betamatic V counter.

### 2.2 Surfactants

Two anionic surfactants as used in the commercial suspension concentrate formulation of triticonazole for wheat seed treatment, 'Soprophor' FLK and 'Supragil' MNS90 and seven alkylphenolethoxylate nonionic micellar surfactants were studied. 'Soprophor' FLK is a phosphate tristyrylphenol ethoxylate anionic micellar surfactant, and 'Supragil' MNS90 is a sodium alkyl-naphthalenesulfate anionic nonmicellar surfactant. 'Triton' X100 is an octylphenol ethoxylate that was chosen for its good solubilization properties and its reported ability to reduce the sorption of poorly soluble organic compounds. 'Triton' N101 (BC9) and 'Igepal' BC5, BC8, BC14, BC17 and BC40 surfactants are nonylphenol ethoxylates of varying numbers of ethoxylate functional units (indicated by the BC number). They were chosen in order to test the influence of increasing the polarity of the surfactant, and hence its HLB, by increasing the length of the ethoxylate polar chain. 'Triton' surfactants were purchased from Sigma-Aldrich Chimie; all other surfactants were furnished by Rhône-Poulenc Agro. All surfactants were used as technical grade. The surfactant solutions were prepared by solubilizing the surfactants in water under ultrasound.

### 2.3 Soil

The soil (typic Eutrochrept) was sampled in the surface layer (0-20 cm) of a continuous wheat experimental plot located at Grignon (France). It had a pH in water of 8.2, with (g kg<sup>-1</sup> of dry soil): 291 clay, 540 silt, 145 sand, 24 lime and 10.4 organic C. Soil samples were air dried and passed through a 2-mm sieve. The soil residual gravimetric water content was 3.6%.

### 2.4 Triticonazole sorption isotherms

A batch equilibrium procedure was used to obtain triticonazole sorption isotherms at 22(±1)°C. [ $^{14}C$ ]triticonazole aqueous solutions (10 ml) were added to soil (5 g) in glass centrifuge tubes (25 ml) with Teflon caps. After 24 h shaking, the samples were cen-

trifuged at 8000*g* for 15 min and the triticonazole concentration in solution at equilibrium,  $C_e$  was calculated from measurement of the radioactivity in the supernatant. The amount of triticonazole sorbed was determined by difference between the initial and equilibrium concentrations in solution. The whole experiment was replicated twice. The same procedure was used to measure triticonazole sorption isotherms in the presence of FLK or MNS90 surfactants at 80 mg litre<sup>-1</sup>.

The sorption isotherms were plotted as the amount of pesticide sorbed ( $x/m$ , mg kg<sup>-1</sup> dry soil) versus the equilibrium concentration  $C_e$  (mg litre<sup>-1</sup>). Freundlich empirical parameters  $K_f$  and  $n_f$  were estimated using a least-square non-linear regression method from the Freundlich equation:

$$x/m = K_f C_e^{n_f} \quad (1)$$

The linear sorption partition coefficient  $K_d$  was calculated by linear curve fitting from the equation:

$$x/m = K_d C_e \quad (2)$$

and the corresponding  $K_{OC}$  value was calculated from the relationship:

$$K_{OC} = K_d (\text{fraction of soil organic C})^{-1} \quad (3)$$

## 2.5 Determination of surfactant CMC

The initiation of micelle formation in solution is indicated by the minimum surfactant concentration at which the surface tension ceases to decline. Measurement of the CMC in water was performed using a Krüss Processor Tensiometer Model K12 with a platinum plate (wetting length 40.0 mm, length 19.9 mm, thickness 0.10 mm). Surface tension was first measured in water, and then the concentration of the surfactant in solution was increased logarithmically by adding appropriate amounts of a concentrated surfactant stock solution. Measurements were made until the increase in surfactant concentration did not cause further decrease in the surface tension. Surfactant stock solution concentrations were 200 mg litre<sup>-1</sup> for BC5, 500 mg litre<sup>-1</sup> for BC8, 1000 mg litre<sup>-1</sup> for X100, N101 and FLK, 2000 mg litre<sup>-1</sup> for BC14 and BC17 and 10 000 mg litre<sup>-1</sup> for BC40. Plots of the surface tension as a function of the logarithm of surfactant concentration permitted the graphical determination of the CMC of the surfactants.

## 2.6 Surfactant sorption on soil

A batch method was used to evaluate the sorption of the surfactants on soil. Thirty grams of soil and 60 ml of

surfactant solutions with concentrations ranging from 0.1 to 50 000 mg litre<sup>-1</sup> were mixed in 250-ml centrifuge tubes, shaken for 24 h at 22(±1)°C, and then centrifuged at 8000*g* for 15 min. Fifty millilitres of the supernatant were pipetted, and surface tension was measured using the Krüss K12 tensiometer. The minimum surfactant concentration required to initiate micelle formation in the soil–water system was determined graphically as previously described.

The amount of surfactant sorbed on soil,  $x/m$ , can be assessed directly by surface tension measurements for surfactant concentrations less than that required to attain the CMC in the soil–water system. The concentration in solution at equilibrium ( $C_e$ ) for a given initial concentration ( $C_i$ ) can be determined graphically from the curves of surface tension versus concentration by measuring the surface tensions of the surfactant solutions before and after equilibration with the soil and determining the corresponding concentrations  $C_i$  and  $C_e$  from the curves. As described for triticonazole sorption, the amount of surfactant sorbed was determined by difference between the initial and equilibrium concentrations in solution, and the surfactant  $K_d$  values were estimated by linear fitting from the sorption isotherms.

## 2.7 Triticonazole sorption in presence of surfactants

Triticonazole sorption studies in the presence of surfactant additives were performed using the same batch equilibrium procedure as previously described, with a single initial concentration of triticonazole for 5 mg litre<sup>-1</sup>. The initial concentrations of the surfactants were chosen as a function of their CMC in water, in order to obtain concentrations below and above their water CMC while remaining at doses representative of formulation field application rates. As an exception, the concentrations of the two most hydrophobic nonylphenol ethoxylates were chosen an order of magnitude higher. FLK and MNS90 concentrations ranged from 0.1 to 200 mg litre<sup>-1</sup>, BC5 and BC8 concentrations were 1000 and 10 000 mg litre<sup>-1</sup>, while BC14, BC17 and BC40 concentrations were 100 and 1000 mg litre<sup>-1</sup>. Finally, X100 and N101 concentrations ranged from 2.5 to 2500 mg litre<sup>-1</sup>. The results were expressed as the percentage of sorbed triticonazole in the presence of the surfactants relative to triticonazole sorption without surfactant.

The change in soil organic carbon content resulting from the surfactant sorption on soil was calculated from the estimates of the amount of sorbed surfactant, converted to amount of carbon sorbed. The new value of soil fractional organic carbon content was then used to calculate the corresponding  $K_{OC}$  for triticonazole sorption in the presence of surfactant.

### 3 RESULTS AND DISCUSSION

#### 3.1 Surfactant aqueous CMC

The aqueous CMC of the selected micellar surfactants in soil-free systems determined from surface tension measurements, along with molecular weights and HLB of the surfactants, are listed in Table 1. The CMC of 151 mg litre<sup>-1</sup> for 'Triton' X100 is in the range of reported values for this surfactant which range from 105 to 195 mg litre<sup>-1</sup>.<sup>12-15</sup> The CMC values of the nonylphenol ethoxylates ranged from 13 to 324 mg litre<sup>-1</sup>, and were inversely related to the hydrophobicity of the surfactants. CMC increased with the number of polar ethoxylates groups, hence with increasing HLB. This was not surprising since surfactants with lower HLB are in general more efficient at micelle formation.<sup>9</sup> A plot of the nonylphenol ethoxylate surfactants' CMC versus surfactant HLB (Fig. 1), including our results along with reported values for BC9.5, BC15, BC20 and BC50 nonylphenol ethoxylates,<sup>19</sup> shows that our results are consistent with other published results for the same surfactant family, with a strong, positive correlation

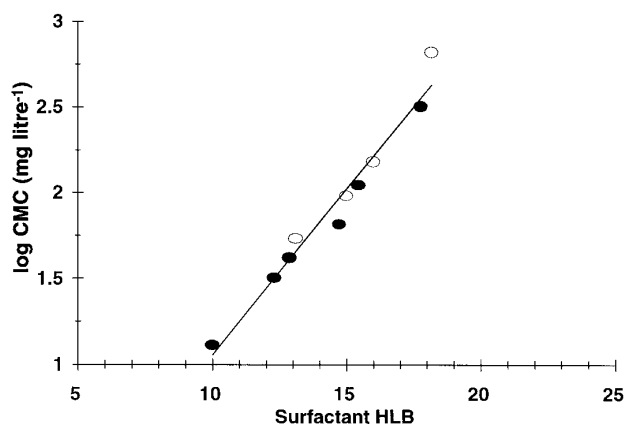


Fig. 1. Relation between (●) measured water CMC and (○) water CMC reported by Schick<sup>19</sup>, and HLB of nonylphenolethoxylate surfactants. Correlation as  $\log \text{CMC} = 0.19 \text{ HLB} - 0.9$  is represented in the line.

between the CMC and HLB of the surfactants ( $\log \text{CMC} = 0.19 \text{ HLB} - 0.9$ ). Finally, 'Soprophor' FLK CMC was measured at 48 mg litre<sup>-1</sup>

#### 3.2 Surfactant sorption

The breaks in the surface tension curves of the soil-water systems were not as marked as in the soil-free systems, with more transitional changes in the surface tension of the aqueous phase (Fig. 2); consequently, measurements of the apparent CMC of the surfactants in soil-water systems were less accurate. This may be attributed to the presence of soluble soil components affecting the surface tension of these systems.<sup>16</sup> However, the right shift of the surface tension curves of the surfactants in the soil-water systems compared to the soil-free systems indicates high sorption on soil of all the surfactants, and shows that the concentrations necessary to initiate micelle formation would be considerably higher in the soil-water systems. Similar strong sorption of Triton X100, Igepal CA-720 (C<sub>8</sub>PE<sub>12</sub>), Tergipol NP-10 (C<sub>9</sub>PE<sub>10.5</sub>), and other alkyl-phenolethoxylates and alkylethoxylates on soil has been reported.<sup>14,20</sup> Estimated ranges of values for the apparent CMC in soil together with estimated averaged  $K_d$  values of the surfactants are listed in Table 2. The highest CMC and  $K_d$  of the nonionic surfactants were found for the most hydrophobic nonylphenol ethoxylates, i.e. BC5 and BC8, and N101 (BC9), suggesting that sorption of the anionic surfactants would probably be related to hydrophobic interactions of the surfactant hydrophobic moiety (alkyl chain) with soil organic matter. Other results of nonylphenol ethoxylate C<sub>9</sub>PE<sub>10</sub> sorption on three soils of varying organic matter content also indicate that sorption of the alkyl-phenolethoxylates is associated with organic matter.<sup>21</sup>

A plot of the nonylphenol ethoxylates'  $K_d$  versus HLB of the surfactants (Fig. 3) shows an increase in  $K_d$  with surfactant HLB until a maximum sorption value is attained with N101 (HLB = 12.9), followed by a contin-

TABLE 1  
Critical Micelle Concentrations (CMC) of Surfactants in Water

Surfactant	Triton X100	Igepal BC5	Igepal BC8	Triton N101	Igepal BC14	Igepal BC17	Igepal BC40	Soprophor FLK
Symbol	C <sub>8</sub> PE <sub>9.5</sub>	C <sub>9</sub> PE <sub>5</sub>	C <sub>9</sub> PE <sub>8</sub>	C <sub>9</sub> PE <sub>9</sub>	C <sub>9</sub> PE <sub>14</sub>	C <sub>9</sub> PE <sub>17</sub>	C <sub>9</sub> PE <sub>40</sub>	
Relative molecular mass	624	440	572	638	836	968	1980	1350
HLB		10	12.3	12.8	14.9	15.8	17.8	16
CMC <sup>a</sup> (mg litre <sup>-1</sup> )	151	13	32	42	66	112	324	48
CMC <sup>a</sup> (μmol litre <sup>-1</sup> )	242	30	56	68	79	116	164	36

<sup>a</sup> Determined graphically from the surface tension/log concentration curves

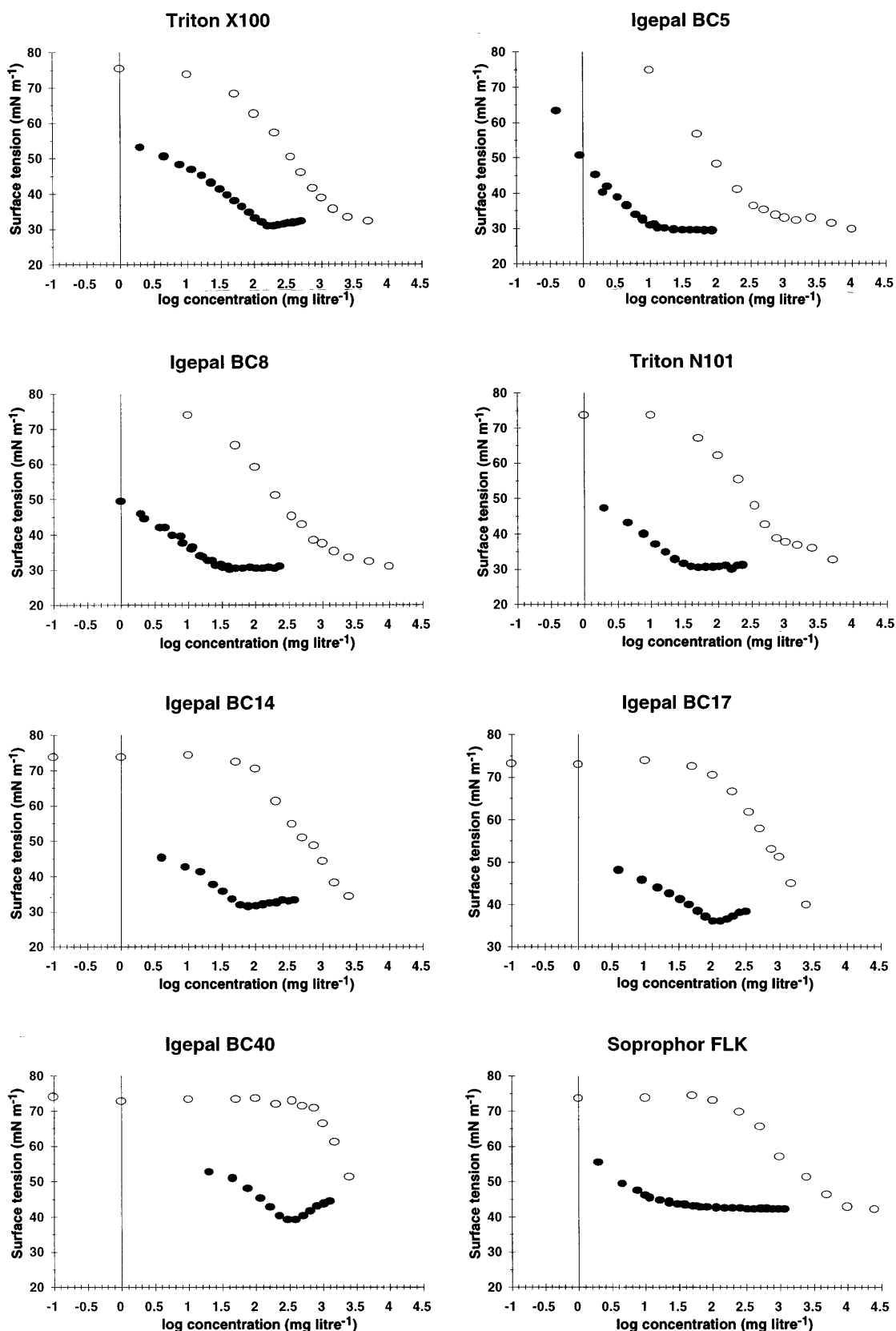


Fig. 2. Surface tensions of surfactants in (●) water and (○) soil-water systems.

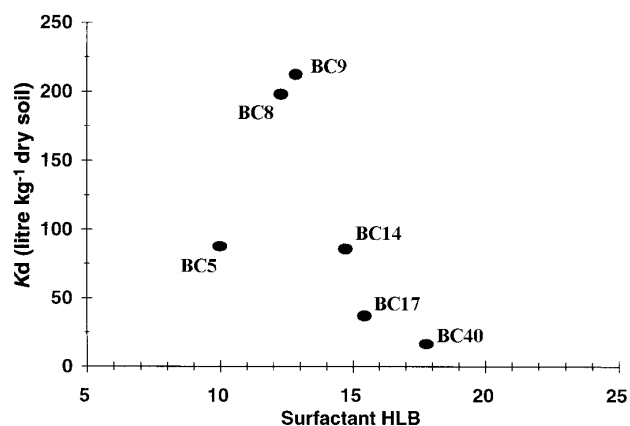


Fig. 3. Relation between estimated average  $K_d$  for sorption of the nonylphenolethoxylate surfactants on Grignon soil and HLB of the surfactants.

uous decrease of  $K_d$  for higher HLB and increasing number of ethoxylate units. Thus, for this series of nonylphenol ethoxylate surfactants, a maximum affinity for interaction with the soil organic surfaces would be attained around HLB 13. The decrease in sorption that is observed when the HLB is further increased shows that the affinity of the surfactant for the soil surfaces decreases when the hydrophilic chain of the surfactant increases, which further supports the hypothesis of sorption of the nonionic surfactants governed by hydrophobic interactions with soil organic matter. Under this condition, the relatively low  $K_d$  estimated for sorption on soil of BC5 and BC8, the most hydrophobic surfactants, is not expected. The aggregation number ( $N_a$ ) of the surfactants increases when HLB decreases.<sup>18</sup> The  $N_a$  value reflects the affinity between monomers of the surfactant, and thus the ability for self-association and formation of micelles. A high  $N_a$  value for BC5, and to a lesser extent for BC8 may result in preferential surfactant-surfactant interactions rather than surfactant-soil surface interactions, and formation of micelles below the CMC.<sup>22</sup> Similar trends in the influence of the HLB of a series of alkylphenolethoxylates were reported for the solubilization of non-aqueous-phase liquids contaminants.<sup>11,18</sup> It is thus suggested that surfactant self-affinity, as indicated by the  $N_a$ , and number of ethoxylate units are major parameters when hydrophobic interactions are considered, with soil sur-

faces (sorption) or with hydrophobic compounds (solubilization). In such systems, a maximum of affinity at an optimal HLB value may be expected for a series of alkylphenolethoxylate surfactants.

Surprisingly, sorption of the anionic surfactant FLK was also extremely important, and its apparent CMC in the soil-water system was approximately 10 000 mg litre<sup>-1</sup>, more than 200-fold its water CMC. Anionic surfactant sorption onto the negatively charged soil surface is usually expected to be minimal. A study of the anionic surfactant sodium dodecyl sulfate showed a less than three-fold increase of the apparent CMC of the surfactant in the presence of soil.<sup>23</sup> Other authors have reported very weak sorption of linear alkylbenzene sulfonate (LAS) on four soils at surfactant concentrations below 100 mg litre<sup>-1</sup>, and they concluded that this arose from specific site surface interactions by the sulfonate hydrophilic head on clay minerals.<sup>24</sup> However, these authors also reported exponentially increasing sorption at high LAS concentrations, which they attributed to sorption of hemi-micelles (admicellization) onto soil through hydrophobic interactions. The same kind of process may explain the strong sorption of FLK at high concentrations.

### 3.3 Surfactant influence on triticonazole sorption

Triticonazole sorption isotherms on Grignon soil, alone and in the presence of surfactants, are presented in Fig. 4. The sorption isotherm of triticonazole is characterized by a high  $K_f$  of  $4.61 \pm 0.20$ , indicating strong sorption, and an  $n_f$  of  $0.87 (\pm 0.02)$ , indicating dominating non-specific interaction mechanisms such as solute partitioning on soil organic matter. Consequently, use of a linear partition coefficient  $K_d$  is justified. An averaged  $K_d$  value of  $4.35 (\pm 0.08)$  litre kg<sup>-1</sup> was calculated, which corresponds to a  $K_{OC}$  of 418 litre kg<sup>-1</sup>. Similar  $K_{OC}$  values were obtained for the sorption of triticonazole on different English soils (Rhône-Poulenc Agro, pers. commun.).

Triticonazole sorption was not significantly modified by the presence of the anionic surfactants used in the commercial formulation, as evidenced in Fig. 4 and Table 3. Triticonazole sorption isotherms in systems

TABLE 2  
Estimated Range for the CMC and Averaged Sorption  $K_d$  of Surfactants in Soil-Water systems

Surfactant	Triton X100	Igepal BC5	Igepal BC8	Triton N101	Igepal BC14	Igepal BC17	Igepal BC40	Soprophor FLK
CMC <sup>a</sup> (g litre <sup>-1</sup> )	2.5–3.5	9.0	7–11	12.5	3.2–4.0	3.5–4.0	> 5	10.0
$K_d$ (litre kg <sup>-1</sup> )	11 ( $\pm 1$ )	88 ( $\pm 10$ )	199 ( $\pm 23$ )	213 ( $\pm 37$ )	86 ( $\pm 5$ )	37 ( $\pm 6$ )	17 ( $\pm 3$ )	216 ( $\pm 20$ )

<sup>a</sup> Determined graphically from the surface tension/log concentration curves

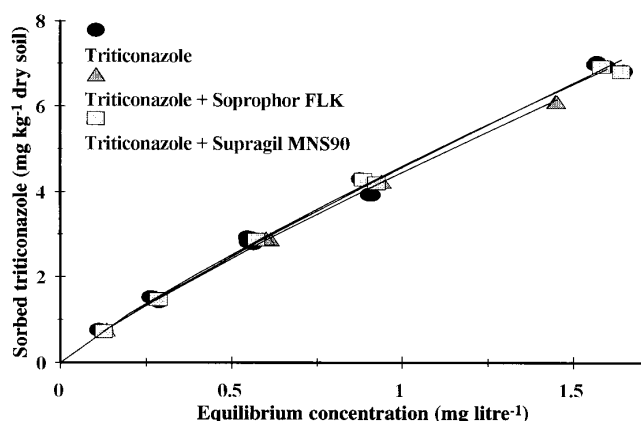


Fig. 4. Equilibrium sorption isotherms of [ $^{14}\text{C}$ ]triticonazole alone and in the presence of 'Soprophor' FLK and 'Supragil' MNS90 anionic surfactants at  $80 \text{ mg litre}^{-1}$ .

containing  $80 \text{ mg litre}^{-1}$  of these surfactants were identical to the isotherm in a surfactant-free system.  $K_f$  and  $n_f$  Freundlich values of  $4.48(\pm 0.11)$  and  $0.88(\pm 0.01)$  respectively for FLK addition, and  $4.60 \pm (0.13)$  and  $0.89(\pm 0.01)$  for MNS90 were extremely close to those for triticonazole alone. Modification of sorption of hydrophobic organic compounds by surfactants usually occurs at concentrations above the CMC, when a surfactant micellar phase is considered.<sup>22,25,26</sup> Hence, our results are not surprising for MNS90 non-micellar surfactant. In the case of FLK, the higher concentrations of 80 and  $200 \text{ mg litre}^{-1}$  added to the system were above the CMC. However, strong sorption of the surfactant on soil, as previously evidenced, increased significantly the concentration required to achieve micellization in the soil solution. Thus, all the initial concentrations of FLK tested resulted in concentrations in the soil-water

systems lower than the CMC. Much higher amounts would be necessary to attain the CMC, but this would prove unrealistic in pesticide formulations.

Similarly, strong sorption of the other surfactants on soil removed a major part of the surfactant molecules from the soil solution. Concentrations well below the CMC would be expected in the soil solution for all combinations except for the highest initial concentrations of X100, N101, BC5 and BC8, where near-CMC concentrations in soil solution would be attained. Triticonazole sorption on soil was little decreased or not affected in the presence of low concentrations of the surfactants, whereas the presence of greater amounts of the most hydrophobic surfactants resulted in a near 50% increase in the sorption of triticonazole (Table 3). Enhanced solubility of the poorly soluble dichlobutrazol triazole fungicide in solutions of BC8 has been reported,<sup>27</sup> and thus there would be a potential for reduction of the sorption of other hydrophobic triazole compounds in soil. However, this author used high surfactant concentrations of 100 and  $200 \text{ g litre}^{-1}$ , which are not representative of agricultural application rates. Dilute nonionic surfactants may show no significant effect on pesticide sorption,<sup>7</sup> when most of the surfactant would presumably be sorbed, while not significantly increasing soil organic carbon content. Other authors reported an increase in the sorption of moderately water-soluble and of hydrophobic compounds in soil-water systems at concentrations of Triton X100 lower than the CMC.<sup>16</sup> This was attributed to an increase in the soil organic carbon content due to surfactant sorption, which favoured the partitioning of the hydrophobic molecules.

Sorption of the alkylphenolethoxylate surfactants on soil is likely to modify the properties of the soil surfaces.

TABLE 3  
Influence of Different Concentrations of Surfactants on the Sorption of [ $^{14}\text{C}$ ]Triticonazole

Anionic surfactants <sup>a</sup>			Alkylphenolethoxylate Triton surfactants			Nonylphenolethoxylate Igepal surfactants				
Soprophor FLK		Supragil MNS 90								
Concentration ( $\text{mg litre}^{-1}$ )	Sorption (% control)		Concentration ( $\text{mg litre}^{-1}$ )	Sorption (% control)		Concentration ( $\text{mg litre}^{-1}$ )	Sorption (% control)			
0.1	100									
1	99	97	2.5	98	100	100		95	100	103
5	99		25	97	99					
10		96	50	96	99					
20	97		250	94	97	1000	109	97	91	92
50		101	500	92	92					101
80	98		2500	127	113					
100		100				10000	151	166		
200	96	102								

<sup>a</sup> Surfactants used in commercial triticonazole formulation.

**TABLE 4**  
Triticonazole Sorption  $K_d$  and  $K_{oc}$  Values in Grignon Soil as Influenced by the Presence of Different Concentrations of Surfactants

Surfactant	None	Triton X100		Triton N101		Igepal BC5		Igepal BC8	
Concentration (g litre <sup>-1</sup> )	—	0.25	2.5	0.25	2.5	1	10	1	10
Carbon (%)	1.04	1.07	1.30	1.07	1.34	1.17	2.33	1.16	2.28
Triticonazole $K_d$ (litre <sup>-1</sup> kg <sup>-1</sup> )	4.35	4.17	5.15	4.02	6.24	5.05	11.77	4.19	19.74
Triticonazole $K_{oc}$ (litre <sup>-1</sup> kg <sup>-1</sup> )	418	389	396	376	466	432	505	361	866

At low concentrations, the nonionic surfactants would directly sorb onto the soil surfaces through hydrophobic interactions of the surfactant alkyl chain with soil organic matter. The hydrophilic heads of the surfactants would extend in solution and thus lower the affinity of triticonazole for the soil surfaces. This may explain the slight decrease in triticonazole sorption to soil that was observed in our systems. However, at higher concentrations, the soil surfaces may be completely covered by a monolayer of surfactant, and the additional surfactant monomers may sorb on the monolayer of hydrophilic heads. This would result in a bilayer of surfactant on the soil surfaces with the surfactant hydrophobic tails sticking out in the aqueous phase, which would considerably enhance the sorption of triticonazole on soil surfaces as observed.

Estimates of the modifications of soil fractional organic carbon content after addition of the more lipophilic surfactants (Triton X100, Triton N101, Igepal BC5 and BC8), and  $K_d$  and  $K_{oc}$  partition coefficients for triticonazole sorption in these soil-surfactant systems, are listed in Table 4. Addition of Igepal BC5 and BC8 surfactants at 10 g litre<sup>-1</sup> more than doubled the soil organic carbon content from an initial 1.04% to an approximate 2.3%. These results agree with the observed increases in triticonazole sorption when applied with these surfactants, since triticonazole sorption was related to soil organic matter content, and would increase with soil fractional organic carbon content. Compared to the  $K_d$  values, the calculated  $K_{oc}$  values for triticonazole sorption appeared much closer for all triticonazole-surfactant-soil combination systems. This confirms the hypothesis of an increase in triticonazole sorption on soil surfaces mediated by the sorption of the hydrophobic surfactants.

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